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On calculation of free energy due to Coulombian and hard core potentials

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To investigate the thermodynamic behaviour of assembly of charged particles in a continuous medium with dielectric constant ϵ, the calculation of free energy for Coulombian interaction and also for short-range interaction are important. In the present paper this is done by using a distribution formula derived by Dutta (1966). For experimental verification the activity-coefficients are calculated from the expression for free energy obtained here and they are compared with the experimental results.

1. INTRODUCTION

To consider the thermodynamic behaviour of assembly of charged particles in a continuous medium like ions of strong electrolytes in solution, it is seen that due attention should be given to the contribution of short-range forces along with the Coulombian forces. The interaction forces of Vander Waal type are supposed to consist of two forces, one repulsive and the other attractive. The simplest model of the repulsive part for this type of forces is hard core. A simple method for discussion of short-range and long-range forces are seen in the papers of Dutta (1947, 1948, 1951, 1952, 1959). Later Dutta (1966) also proposed a modified technique in which notion of coarse-graining has been employed for taking into account of hard core potential in addition to other potentials. The above method of taking into account of hard core potential has a wider acceptance in the literature of Statistical Physics (c.f. Rullo 1969). But the result of Dutta (1966) has never been used in calculation of any problem of physical interest. In calculations of free energy for an assembly of charged particles the method in which the hard core potentials are taken into account by the formula of Dutta-Bagchi (1950), cannot be applied in cases of concentrated solutions of strong electrolytes, because in many cases $nb > 1$ whereas the calculations should be made when $nb < 1$, where n is the number density and b is the exclusion volume. It appears that if the result of Dutta (1966) is used in calculation, the above difficulty can be avoided.

In this paper attempts have been made to use the result of Dutta (1966) in calculation of free energy in the assembly of charged particles in a continuous medium and as an application the expression for free energy has been used in calculating the activity coefficients of strong electrolytes in solution.

In present calculation no logical inconsistency in considering $nb > 1$ has been faced and the agreement obtained in the experimental case is not inferior in any case to those calculated in earlier works.

2. Calculation of Free Energy

In the case of assembly of charged particles if it is assumed that the average minimum approach of oppositely charged particles is very small compared to that of the particles of like charges i.e., $b_{+-} \ll b_+$ and b_-, then the distribution formula of Dutta (1966) is given by

$$n_\pm = \frac{1}{b}\left[\frac{1}{\exp(\nu_\pm + Z_\pm e_\pm \psi/kT)-1} - \frac{(r_\pm+1)}{\exp\{(r_\pm+1)(\nu_\pm + Z_\pm e_\pm \psi/kT)\}-1}\right], \quad \ldots (1)$$

where $n_\pm$ are the number densities of positively and negatively charged particles with charges $z_+ \cdot e_+$ and $z_- \cdot e_-$ respectively at a point where the mean electric potential is ψ, $r_\pm = [b/b_\pm]$ is the integer just less than $b/b_\pm$, b being the volume of a cell and b_+, b_- the exclusion volumes of positively and negatively charged particles, so that a cell may remain vacant or may be occupied utmost by $r_\pm$ particles only. $\nu_\pm$ are the parameters of the distribution and k, T have their usual significances.

Here it is assumed that $r = 2$, so that

$$n_\pm = \frac{1}{b}\left[\frac{1}{\exp(\nu_\pm \pm Z_\pm e\psi/kT)-1} - \frac{3}{\exp\{3(\nu_\pm \pm Z_\pm e\psi/kT)\}-1}\right]. \quad \ldots (2)$$

The charge density ρ at any point in the assembly is given by

$$\rho = e(n_+ Z_+ - n_- Z_-). \quad \ldots (3)$$

Thus for large and small values of ψ we have

$$\rho_{\psi \sim \infty} = -\frac{2Z-e}{b}, \quad \ldots (4)$$

$$\rho_{\psi \sim 0} = -\frac{e^*}{bkT}\,\Sigma A_i Z_i^2 \psi, \quad \ldots (5)$$

where

$$A_i = 3B_i + \frac{2(B_i-1)}{C_i-1} - B_i, \quad \ldots (6)$$

$$B_i = n_i^0 b, \quad \ldots (7)$$

$$C_i = [2(3B_i+1)^{\frac{1}{2}}\cos\theta_i + 1]/3B_i, \quad \ldots (8)$$

$$\cos 3\theta_i = \frac{27B_i^3 - 54B_i^2 + 9B_i + 2}{2(3B_i+1)^{3/2}}, \qquad \ldots (9)$$

n_i^0 being the stochiometric number density of i-th particle in the assembly.

The Poisson equation in dimensionless variables then reduces to

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2 \frac{d\lambda}{d\xi}\right) = \lambda \qquad \text{when } \lambda \sim 0, \qquad \ldots (10)$$

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2 \frac{d\lambda}{d\xi}\right) = m_+ \qquad \text{when } \lambda \sim \infty_\pm, \qquad \ldots (11)$$

where

$$\lambda = \frac{e\psi}{kT}, \qquad \xi = \varkappa r,$$

$$\left[\frac{\Sigma A_i Z_i^2}{b}\right], \qquad m_\pm = \frac{2Z_\mp}{\Sigma A_i Z_i^2}.$$

The approximate solutions λ_1 and λ_2 of the eqs. (10) and (11) subject to the boundary conditions

as $$r \to \infty, \quad \psi \to 0 \qquad \ldots (12)$$

and

$$\int_{\delta: r=a} \frac{d\psi}{dr}\, dS = -\frac{4\pi}{\epsilon} Z_+ e$$

and also satisfying the 'method of fit'

$$(\lambda_1)_{\xi_1} = m_+ = (\lambda_2)_{\xi_1}, \qquad \ldots (14)$$

$$\left(\frac{d\lambda_1}{d\xi}\right)_{\xi_1} = \left(\frac{d\lambda_2}{d\xi}\right)_{\xi_1}, \qquad \ldots (15)$$

whore ξ_1 is the point at which transition from λ_2 to λ_1 takes place (Sengupta 1968). are given by

$$(\lambda_\pm)_1 = \frac{Z_\pm}{\epsilon kT} \frac{e^2 \varkappa e^{\xi a_\pm}}{1+\xi a_\pm} \frac{e^{-\xi}}{\xi}, \qquad \ldots (16)$$

$$(\lambda_\pm)_2 = m_\pm \left[\frac{\xi^2}{6} + \frac{1}{2}\{1-(1+g_\pm)^{2/3}\} + \frac{g_\pm}{3\xi}\right], \qquad \ldots (17)$$

where

$$g_\pm = 3\left[\frac{Z_\pm e^2 \varkappa}{m_\pm \epsilon kT} + \frac{(\varkappa a_\pm)^3}{3}\right]. \qquad \ldots (18)$$

In deducing the expression for free energy three distinct cases are considered.

(i) When the surface potential of both positively and negatively charged particles is given by λ_1 we have for the additional free energy (available electric work)

$$(\omega_\pm) = -\frac{Z_\pm{}^2 e}{\epsilon}\int_0^1 \frac{e\kappa x^2}{1+\kappa a x}\,dx = -\frac{(Z_\pm e)^2}{}\,\kappa\theta_\pm, \qquad \ldots (19)$$

where

$$\theta_\pm = \left[\frac{(\kappa a_\pm)^2}{2} - \kappa a_\pm + \ln(1+\kappa a_\pm)\right] /(\kappa a_\pm)^3. \qquad \ldots (20)$$

Thus the total additional free energy for all the particles in the assembly is given by

$$W = n_+\omega_+ + n_-\omega_- = -\frac{e^-}{\epsilon}\kappa[n_+ z_+{}^2\theta_+ + n z_-{}^2\theta_-]. \qquad \ldots (21)$$

(ii) When the surface potential of both positively and negatively charged particles is given by λ_2 we have,

$$(\omega_\pm) = \frac{kTm}{2} \pm z_\pm[\tfrac{1}{2}(\kappa a_\pm)^2 + P + \phi_\pm(g_\pm)], \qquad (22)$$

where

$$P = \tfrac{1}{2} + \frac{1}{\sqrt{3}}\tan^{-1}\sqrt{3} - \tfrac{1}{2}\log_e 3 = \cdot 5551 \qquad (23)$$

and

$$\phi_\pm(g_\pm) = \tfrac{1}{2}\ln[(1+g_\pm)^{2/3} + (1+g_\pm)^{1/3} + 1]$$

$$-\tfrac{1}{2}(1+g_\pm)^{2/3} - \frac{1}{\sqrt{3}}\tan^{-1}\frac{2(1+g_\pm)^{1/3}+1}{\sqrt{3}}. \qquad (24)$$

(iii) When the surface potential of positively charged particle is given by λ_1 and negatively charged particle is given by λ_2 we have,

$$W = -n_+\frac{(z_+ e)^2}{\epsilon}\kappa\theta_+ + n_- z_- \frac{kTm_-}{2}[\tfrac{1}{2}(\kappa a_-)^2 + P + \phi_-]. \qquad \ldots (25)$$

3. Experimental Verification

For experimental verification mean activity-coefficients of ions of strong electrolytes in solution $f_\pm$ are calculated from the experession for free energy by the formula

$$\ln f_\pm = \frac{1}{kT}\frac{z_-\dfrac{\partial W}{\partial n_+} + z_+\dfrac{\partial W}{\partial n_-}}{z_+ + z_-} \qquad \ldots (26)$$

and they are compared with the mean activity-coefficients of some 1–1 and 2–1 electrolytes in solution, viz., NaCl, KCl, $Ca(NO_3)_2$ etc. as these data are easily available.

Using the formula (21)

$$\ln f_{\pm} = -\frac{e^2\kappa}{\epsilon KT}\frac{z_+z_-}{\Sigma z_i}\left[(1-s)\Sigma z_i\theta_i + \frac{s_\delta}{2}\Sigma\frac{z_i}{1+\kappa a_i}\right], \quad \ldots (27)$$

where

$$s = n_+M_+ + n_-M_-, \quad \ldots (28)$$

$$M_{\pm} = \frac{z_{\pm}^2\frac{\partial A_{\pm}}{\partial n_{\pm}}}{\Sigma A_i z_i^2}. \quad \ldots (29)$$

Numerical values of $-\log f_{\pm}$ calculated at 25°C ($\epsilon = 78{\cdot}6$) from the expression (27) are given in the table below. Here the volume of a cell b is taken to be $2.4/3\pi a^3$, where a is the mean distance of approach of ions.

Table 1

	$-\log f_{\pm}$ for 1-1 electrolytes							
molarity(m)	·1	·2	·3	·5	1	2	3	4
				$a_+ = a_- = 3{\cdot}6$Å				
$-\log f_{\pm}$	·1185	·1515	·1726	·1999	·2341	·2615	·2565	·2485
				$a_+ = a_- = 3{\cdot}9$Å				
	·1162	·1476	·1673	·1922	·2213	·2366	·2225	
				$a_+ = a_- = 4{\cdot}4$Å				
	·1124	·1413	·1588	·1801	·2003	·1952		
	2-1 electrolyte, $a_+ = a_- = 4{\cdot}7$Å							
	·1	·2	·3	·5	·9			
$-\log f_{\pm}$	·3072	·3639	·3946	·4189	·4346			

For the sake of comparison both the theoretical values obtained and also the observed values of some electrolytes in solution are shown in the Figure. The experimental values have been obtained from the compilation of Harned & Owen (1953).

4. Conclusion

The above calculations show that the theoretical results obtained in above form using the distribution formula proposed by Dutta (1966) is a better agreement than those obtained earlier as Dutta & Sengupta (1954) and Sengupta (1956, 1968). It appears that according to the said formula of Dutta $nb_{\pm} < r$, where r is the number of ions the centre of which may come to the surface of

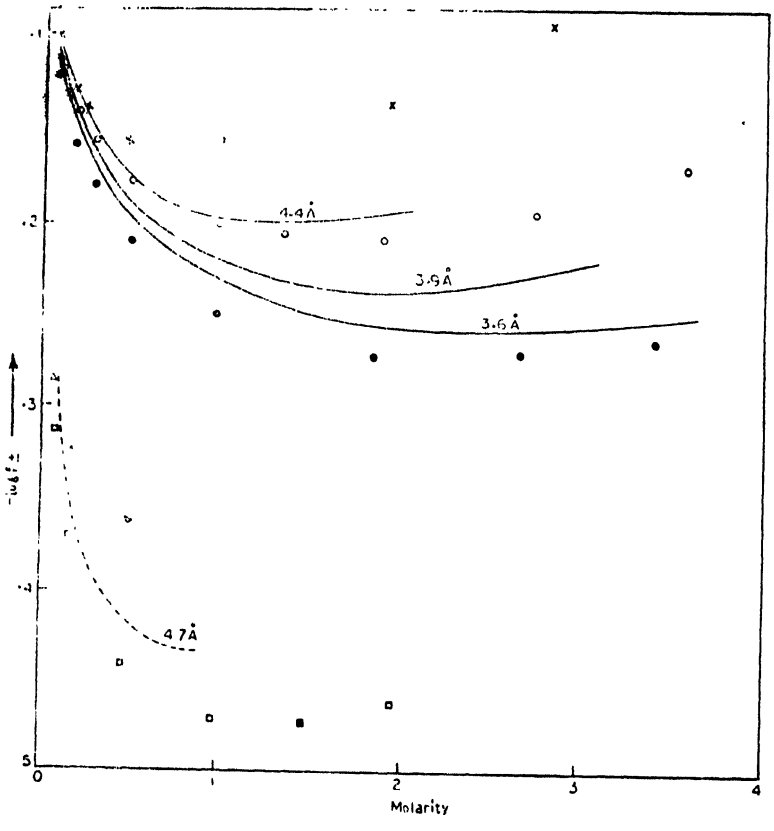

Fig. 1. Log $f_{\pm}$ vs. concentration curves, the continuous lines correspond to 1-1 electrolytes and the dotted lines correspond to 2-1 electrolytes in solution.
The symbols corresponding to experimental values are given as : NaCl—×; KCl—O; CSCl—ϕ; $CaCl_2$—Δ; $Na(No_3)_2$—□; $Sr(No_3)_2$—σ.

volume of exclusion in close packing and so may be applied to a much higher concentration than those of earlier workers, where nb must be less than or equal to 1. Application of this theory to the cases of higher concentration with appropriate higher values of r will be investigated later and will be the subject matter of future communication.

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